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Calorimetric study of the antiferromagnetic ordering in cobalt and nickel garnets

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Abstract : Some calorimetric studies are carried out on polycrystalline specimens of cobalt and nickel garnets in order to determine their magnetic properties using the concepts of the molecular field theory. It is shown that the magnetic properties of the cobalt garnet can be determined applying the molecular field theory while on the contrary for the nickel garnet, which has the same magnetic structure as the cobalt garnet, the molecular field theory is not applicable.

Keywords : Calorimetric study, antiferromagnetic ordering, cobalt and nickel garnets.

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1. Introduction

Belov *et al* [1, 2] investigated the magnetic susceptibility of polycrystalline garnets in which the octahedral sublattices consist, only, of Co^{2+} or Ni^{2+} ions. Authors showed that in these garnets, at 4.2 K, appears an antiferromagnetic ordering due to the $Co^{2+} - Co^{2+}$ and $Ni^{2+} - Ni^{2+}$ internal exchange interactions.

Neutron diffraction studies on $NaCa_2Co_2V_3O_{12}$ (CoVG) and $NaCa_2Ni_2V_3O_{12}$ (NiVG) garnets [3, 4] showed that their magnetic structure is identical and consists of two cubic ferromagnetic sublattices placed antiferromagnetically one inside the other. Authors have determined the spin of the Co^{2+} ion, at 4.2 K, to be $s = 0.8$ which is less than $s = 3/2$ for the free Co^{2+} ion.

Sturge *et al* [5] have studied the EPR of Co^{2+} in $Y_3Ga_5O_{12}$ monocrystal. They showed that, since the spin-orbital splitting parameter λ is approximately equal to 200 cm^{-1} only the lower Kramers doublet, then, may be occupied. Accordingly, to get an information about the magnetic properties of CoVG one can use the spin hamiltonian with effective spin $s = 1/2$, namely,

$$H = -g\mu_B H_{eff} s$$
$$= -2 \sum_{i>j} \hat{s}_i J_{ij} \hat{s}_j \qquad (1)$$

where H_{eff} is the exchange field in the absence of an external magnetic field, g is the splitting factor, μ_B is the Bohr magneton, s is the effective spin, and J_{ij} is the exchange integral.

Neglecting the hyperfine interaction, the spin hamiltonian for the singlet state of ions lying far away from the higher levels can be written in the form,

$$\hat{H} = \mu_B g_{ij} H_i \hat{s}_j + D_{ij} \hat{s}_i \hat{s}_j. \tag{2}$$

The first term of eq. (2) represents the splitting of the levels in an external magnetic field, while the second term represents the splitting of the principal state in the absence of the field.

In NiVG if a trigonal deformation of the octahedral site takes place along the Z-axis, in the absence of the external magnetic field and at 4.2 K, the hamiltonian can be written as,

$$\hat{H} = g \mu_B H_{eff} \hat{s} + D \left[\hat{s}_2^2 - \frac{1}{3} s(s+1) \right] \tag{3}$$

where the coefficient D represents the splitting of the level in the trigonal field. The value of D was measured for NiVG, at 4.2 K, to be 6.79 cm^{-1} [6], while it is equal to 6 cm^{-1} using the EPR technique [5].

In the present work, we have carried out some calorimetric studies on polycrystalline specimens of CoVG and NiVG to get some informations about the antiferromagnetic transitions and exchange interactions in these garnets.

2. Experimental

The investigated specimens are prepared by the usual ceramic technology [7] in the shape of tablets each of diameter 10 mm and height 3 mm. The density of the tablet is determined to be 3.6 gm/cm^3

The specific heat is measured in the temperature range 2-18 K by the method given by Belov *et al* [8]. The temperature is measured by a thermometer of the Allen-Bradley type and is determined by the Clement-Quinell formula [9], i.e.

$$\frac{1}{T} = \frac{A}{\log R} + C \log R + B \tag{4}$$

where A, B and C are constants which can be-determined by calibrating the thermometer using liquid hydrogen and liquid helium.

For measuring the specific heat in an external magnetic field, a superconducting solenoid is used which gives a magnetic field of 45 KOe.

3. Results

Figures 1a and 2a represent the temperature dependence of the specific heats of the cobalt and nickel garnets in the range 2-18 K in the absence of the magnetic field. The λ-anomaly of the specific heats which reflects the antiferromagnetic ordering of Co^{2+} and Ni^{2+} in the B-

sublattice helps us to find the Neel temperatures T_N which are given in Table 1

Table 1. Different parameters used in the present study.

Specimen	$T_N K$	s	$a K^2$	$b\ 10^6 K^3$	g	$Q_p K$	$J_1 K$	$J_2 K$
CoVG	6.42	0.55	27±3	31.1±0.5	5	−17.5	−2.94	−1.81
NiVG	7.90	1.0	61±3	25±0.1	2	−11.0	−1.27	−0.6

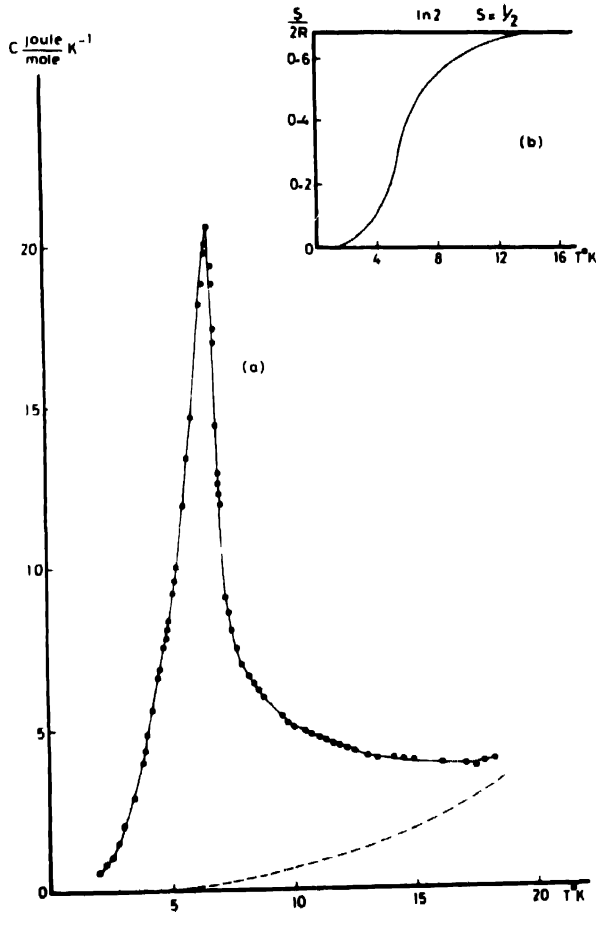

Figure 1. (a) The temperature dependence of the specific heat of $NaCa_2Co_2V_3O_{12}$ garnet (points) and its lattice part (dashes) (b) The entropy temperature dependence of $NaCa_2Co_2V_3O_{12}$.

At low temperatures the garnets under investigation are considered as magnetic insulators, so we can write for the specific heat the relation,

$$C = C_{\text{lattice}} + C_{\text{magnetic}} + C_{\text{nuclear}} \tag{5}$$

However, the value of the nuclear specific heat C_{nuclear} at $T = 2$ K represents only 3% of the whole specific heat of the garnet and it can be neglected in the temperature range 2-18 K. In

this region of temperature, the following relation can be applied

$$\frac{C}{2R} = \frac{a}{T^2} + b\,T^3 \tag{6}$$

where R is the universal gas constant.

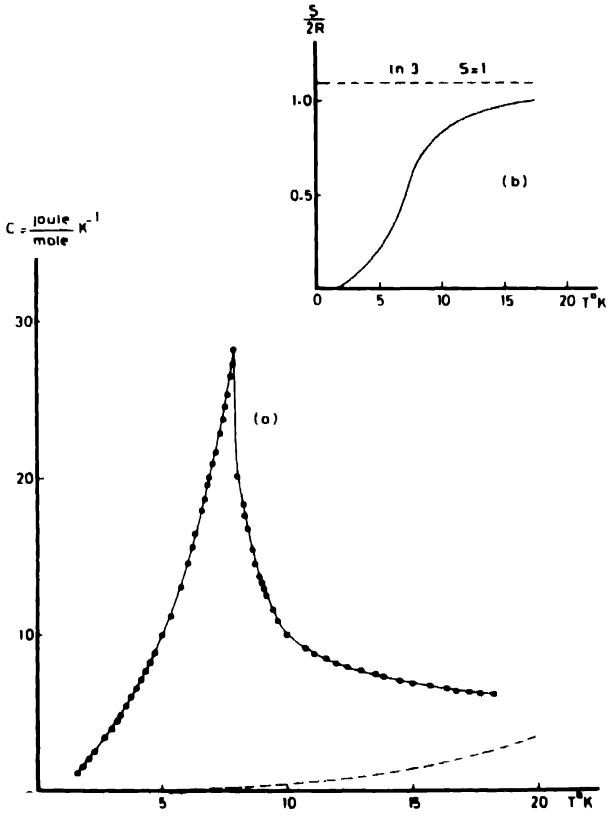

Figure 2. (a) The temperature dependence of the specific heat of $NaCa_2Ni_2V_3O_{12}$ garnet (points) and its lattice part (dashes). (b) The entropy temperature dependence of $NaCa_2Ni_2V_3O_{12}$ garnet

The values of a and b can be obtained from a graphical representation between $\frac{CT^2}{2R}$ and T^5. These values are given in Table 1.

The first term of eq. (6) gives the magnetic part of the specific heat at $T >> T_N$, while the second gives the sublattice part.

Figures 1b and 2b show the temperature dependence of the magnetic entropy of the garnets under study. The determination of the entropy and the internal energy is carried out using the simple relations,

$$\frac{S}{2R} = \int_{T_1}^{T_2} \frac{1}{2R}\,\frac{C_{\text{mag}}}{T}\,dT \tag{7}$$

and $$\frac{E}{2R} = \int_{T_1}^{T_2} \frac{C_{mag}}{2R}\, dT \qquad (8)$$

Here, the limits have been chosen in such a way that $\frac{S}{2R} = 0$ and $T = 0$ and $\frac{E}{2R} = 0$ at $T = \infty$.

The extrapolation to $T = 0\,K$ is done by considering that C_{mag} is proportional to T^3 which results from the theory of spin waves at $T << T_N$.

The change in specific heat at $T > 18$ K is deduced by the temperature square law.

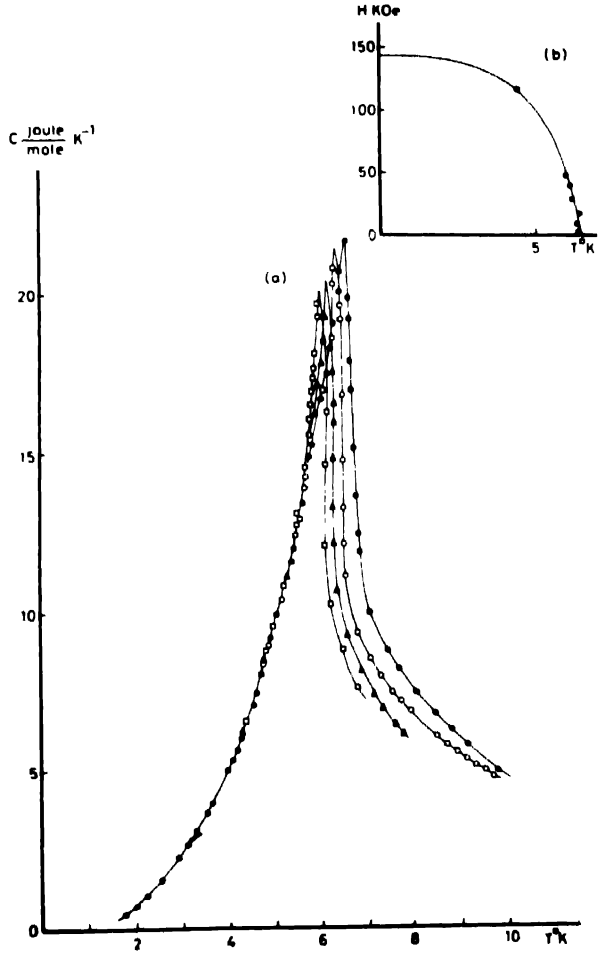

Figure 3. (a) Temperature dependence of the specific heat of $NaCa_2Co_2V_3O_{12}$ garnet in external magnetic field : • H = 0.5, 10, 20 KOe, OH = 30 KOe, ▲ H = 40 KOe, □ H = KOe. (b) Magnetic phase diagram of $NaCa_2Co_2V_3O_{12}$ garnet

Figure 3a shows the relation between the temperature and the specific heat of the $NaCa_2Co_2V_3O_{12}$ garnet in the absence of a magnetic field and in fields of values 20, 30, 40 and 45 KOe.

It is shown from Figure 3a that the temperature dependence of the specific heat at H = 5, 10, and 20 KOe is the same as that found at H = 0. At H = 30 KOe and more, the maximum value of the specific heat decreases and is shifted towards the region of low temperatures. Accordingly, the disturbance of the antiferromagnetic ordering occurs at critical fields of values H_{crit} = 30 KOe at T_N = 6.3±0.05 K, $H_{crit.}$ = 40 KOe at T_N = 6.1±0.05 K, and H_{crit} = 45 KOe at T_N = 6.0±0.05 K. In different magnetic fields, the specific heat versus temperature curves at temperatures lower than 5.2 K, are found to be the same.

However, when using the molecular field theory the g-factor and the paramagnetic Curie temperature must be determined. The Curie temperatures θ_p are obtained from the magnetic susceptibility measurements and the g factors are determined using the effective magnetic moments and the related spin values according to the relation,

$$g = \frac{\mu_{eff}}{\sqrt{s(s+1)}} \tag{9}$$

4. Discussion and conclusions

Applying the molecular field theory the integrals of the exchange interaction for the nearest and next nearest neighbours can be obtained. Smart [10] explained that, in case of antiferromagnetic ordering, the Neel temperature T_N and the Curie temperature θ_p are related to the values of the exchange integrals by the simple relations,

$$T_N = -\frac{2}{3k} s(s+1)\,[z_1J_1 - z_2J_2] \tag{10}$$

and

$$\theta_p = \frac{2}{3k} s(s+1)\,[z_1J_1 + z_2J_2] \tag{11}$$

Our values for J_1 and J_2 of CoVG determined using these relations are in agreement with those reported in literature [6].

According to Abragam and Bleaney [11]; at high temperatures ($T >> T_N$), the magnetic part of the specific heat due to the exchange interactions, can be written in the form

$$C_{exch} = \frac{R}{T^2} \cdot \frac{1}{2} \left[\frac{s(s+1)}{3k}\right]^2 \cdot \sum_{j>i} (J^2_{xx} + J^2_{yy} + J^2_{zz}) \tag{12}$$

i.e. the value $\frac{CT^2}{R}$ is constant for both specimens under investigation.

Using the Heisenberg hamiltonian and considering only the isotropic part of the interaction with the nearest and the next nearest neighbours, one can write

$$\frac{C_{exch}\,T^2}{2R} = \frac{1}{2} \cdot \frac{4\,s^2(s+1)^2}{3\,k^2} \left[z_1J^2_1 + z_2J^2_2\right] \tag{13}$$

where z_1 and z_2 are the numbers of the nearest and the next nearest neighbours respectively.

Substituting the values of J_1 and J_2 (given in Table 1) in eq. (13), we find

$$\frac{C_{exch}\, T^2}{2R} = a = 33\text{K}^2$$

which is in agreement with the experimental results (Table 1).

In order to make a correlation between the molecular field theory and the experiment for CoVG, the magnetic phase diagram must be determined. This can be done by considering the energy levels of the specimen at $T < T_N$ in an external magnetic field H_o using the magnetic structure given in Figure 4.

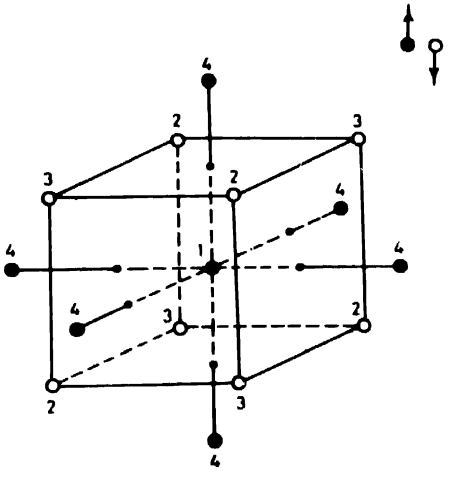

Figure 4. The magnetic structure of $NaCa_2Co_2V_3O_{12}$ and $NaCa_2Ni_2V_3O_{12}$ garnets.

For one atom the internal magnetic energy is given by

$$E_i = -2\, s_i \langle s \rangle (z_1 J_{01} \cos 2\,\phi + z_2 J_{02}) - g\, \mu_B\, s_i\, H_o \cos \phi \tag{14}$$

Neglecting anisotropy the sublattices are inverted in the field of minimum value then rotate at an angle ϕ with increasing the field.

According to the molecular field theory, the interaction of the i-th spin with others can be replaced by the interaction with the average spin $\langle s \rangle$.

For $2N$ atoms we have,

$$E = -2N\, s_i \langle s \rangle (8\, J_1 \cos 2\phi + 6\, J_2) - 2N_g U_B\, s_i\, H_o \cos \phi \tag{15}$$

Simplifying this equation and expressing $\langle s \rangle$ in terms of the saturation magnetisation of the specimen at a given temperature T, we get

$$M_s(T) = 2\, Ng\, \mu_B \langle s \rangle. \tag{16}$$

For the value of the critical fields which disturb the antiferromagnetism, we have

$$H_{crit}(T) = \frac{32\, J_1}{2\, Ng^2\, \mu^2 B} M_s(T) \tag{17}$$

Bearing in mind that the constant of molecular field is given by,

$$\gamma_1 = \frac{2 z_1 J_1}{2N g^2 \mu^2 B}$$

then

$$H_{crit}(T) = -2 \gamma_1 M_s(T) \tag{18}$$

The temperature dependence of the saturation magnetisation can be ecpressed by the usual relation

$$M(T) = M(0) B \left(\frac{g \mu_B s}{kT} H_{eff}\right)$$

where $B(x)$ is the Brillouin function and H_{eff} according to Figure 4, has the expression

$$H_{eff} = M(-\gamma_1 + \gamma_2).$$

The values of the critical fields obtained in this manner are plotted against temperature in Figure 3b (full line). For all values of H and T lying under the curve, the specimen exists in the antiferromagnetic state, while it exists in the paramagnetic state in the area over the curve. The experimental points are also given in the same Figure. These points are obtained by measuring the specific heat of the CoVG at $T = 4.2$ K and $H_{crit} = 120$ KOe. The good agreement between the determined dependence of H_{crit} on T and its experimental dependence indicates that, at $T < T_N$, the magnetic properties of CoVG can be determined applying the molecular field theory.

For nickel garnet, the situation is more difficult. In fact, if in eq. (13) the values of the exchange integrals obtained from relations (10) and (11) are substituted, we find for Ni VG that

$$\frac{CT^2}{2R} = 18 K^2$$

which is much less than the experimental value

$$a = \left(\frac{CT^2}{2R}\right)_{expt} = 61 K^2.$$

In our mind, the strange behaviour of the specific heat of the nickel garnet may be attributed to the fact that the splitting of the principal energy level of Ni^{2+} in the crystal field of the garnet takes place at the value $\frac{D}{k} = 8.7$ K which is comparable with the splitting of the levels due to the exchange field at 0 K ($T_N = 7.9$ K). this situation leads to two important facts. First is that the levels in the exchange field are not equidistant and thus eqs. (10) and (11) can not be applied for the nickel garnet.

It is seen from Figure 2b that the entropy, at T_N, is approximately equal to 0.65 (for $s = 1/2$). This indicates that, at T_N, two levels, only, are occupied. Accordingly, the Curie-Weiss law for s = 1 at temperatures $T > T_N$, is not applicable. The second fact is that, at high temperatures $T >> T_N$, when the splitting due to the exchange field is small, all the

magnetism can be determined by the transitions between the levels separated by an interval $\frac{D}{k} = 8.7$ K.

Abragam and Bleaney [11] gave for the specific heat the relation,

$$\frac{C}{R} = <\left(\frac{W}{K}\right)^2> T^{-2} - <\left(\frac{W}{K}\right)^3> T^{-3} + . \tag{19}$$

In case, if $<W> = 0$, then for $s = 1$ the hamiltonian can be written in the form,

$$\hat{H}_D = D\left[\hat{s}_z^2 - \frac{2}{3}\right] \tag{20}$$

where $s_Z = +1, -1, 0$ ... i.e. in trigonal field we have a system of two energy levels in which $s_Z = 0$ for the lower level, and the upper level is doubley split where $s_Z = \pm 1$.

From eq. (29) we can find that the lower level is characterized by the value $<W_1^2> = \frac{4}{9}D^2$, while the upper level by the value $<W_2^2> = \frac{1}{9}D^2$.

At $T >> T_N$, it can be assumed that the probability of both levels to be occupied is the same, then

$$<W^2> = \frac{1}{2}\cdot\frac{1}{9}D^2 + \frac{1}{2}\cdot\frac{4}{9}D^2 = \frac{5}{18}D^2.$$

In this way, taking $D = 6$ cm $^{-1}$ we find

$$\frac{CT^2}{2R} = \frac{5}{18}\left(\frac{D}{K}\right)^2 = 21\ K^2.$$

Accordingly, the specific heat of the nickel garnet at $T >> T_N$, consists of two parts : one is due to the transitions between levels in the crystal field i.e. a specific heat of the Schottky type. This gives about 30% of the experimental value $\frac{CT^2}{2R} = 61\ K^2$. The other part is due to the exchange interactions $\frac{CT^2}{2R} = 40\ K^2$.

Substituting these values in eq. (13) we can obtain one relation to get the exchange integrals for the NiVG.

In very strong fields, $H_{crit} = 294$ KOe and $T = 4.2$ K, the saturation magnetic moment of the nickel garnet is $M_s = 3.9\ \mu_B$ / mole which is approximately, in agreement with the value $M_s(0) = 2\ N\ g\ \mu_B = 4\ \mu_B$ / mole. The experimental value of M_s leads to the fact that at 4.2 K, the lower level is only occupied. Accordingly, we can substitute the value of the average spin $<s>$ in eq. (15) then use eq. (17) to get the exchange integrals of the NiVG.

By solving eqs. (13) and (17) and substituting the values $(\frac{CT^2}{2R})_{exch} = 40\ K^2$, H_{crit} (4.2 K) = 294 KOe, M_s (4.2 K) = 21.7×10^3 erg/gauss-mole, and $s = 1$ we can get for the nickel garnet

$$\frac{J_1}{k} = -1.27\,K \text{ and } \frac{J_2}{k} = -0.6\,K.$$

This gives an information that the antiferromagnetic phase transition in $NaCa_2Co_2V_3O_{12}$ and $NaCo_2Ni_2V_3O_{12}$ can not be treated using the same theoretical model. This is attributed to the difference in behaviour of the octahedral ions of both garnets (either Co^{2+} or Ni^{2+}) with the crystal field.

Acknowledgment

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